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Influence of the Tungurahua eruption on the ice core records of Chimborazo, Ecuador

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The comparison of two shallow ice cores recovered in 1999 and 2000 from the same place on Chimborazo summit glacier revealed the influence of the coincident Tungurahua volcanic eruption on their stable isotope and chemical records. The surface snow melting and water percolation induced from the ash deposition caused a preferential elution and re-localization of certain ionic species, while the stable isotope records were not very affected. Additionally, the comparison of the ionic amount and some selected ratios preserved along the ice core column reports under which processes the chemical species are introduced in the snow pack, as snow flake condensation nuclei, by atmospheric scavenging or by dry deposition. This preliminary study is essential for the interpretation of the deep Chimborazo ice core, or for other sites where surrounding volcanic activity may disturb the glaciochemical records.

1 Introduction

Mid- and low- latitude glacier ice cores have great potential as environmental and climatic archives. This has been demonstrated by several previous studies in the Andes (e.g. Thompson et al., 1979, 1995, 1998; Ginot et al., 2002; Schotterer et al., 2003; Henderson et al., 1999; Knüsel et al., 2003), in the Alps (e.g. Preunkert et al., 2000; Döscher et al., 1995; Eichler et al., 2000; Schwikowski et al., 1999; Schotterer et al., 1997), in Africa (Thompson et al., 2002) and in Central Asia (e.g. Olivier et al., 2003; Thompson et al., 1997, 2000; Kang et al., 2002; Kreutz and Sholkovitz, 2000). However, as a proxy record, the interpretation of the information recorded in an ice core is far to be trivial. Several processes determine how the climatic and environmental information is written in the ice: origin and recycling of moisture, air masses circulation and mixing, in-cloud scavenging of aerosol particles as condensation nuclei and below-cloud scavenging of particles and gases by ice crystals and snow flakes, dry

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deposition, post-depositional processes etc. As described by Ginot et al. (2001), Stichler et al. (2001), and Schotterer et al. (2004), post-depositional processes in the Andes include surface snow sublimation, surface melting and wind drift. In this study, we investigated the effect of percolation of surface melt water on Chimborazo summit glacier caused by a volcanic eruption in the vicinity, and the implications on the recovered ice core records.

The Chimborazo (6268 m, 1°30' S, 78°36' W) is located on the eastern border of the Occidental Cordillera in Ecuador (Fig. 1). This double-peak inactive volcano (Cumbre Ventimilla and Cumbre Whymper) receives precipitation originating from both West (Pacific Ocean) and East (Atlantic Ocean and Amazon basin) sides, depending to the position of the Inter Tropical Convergence Zone (ITCZ). Thus, the annual precipitation pattern on Chimborazo reflects a varying influence from oceanic and continental air masses with two rainy seasons (February–May and October–November) and two dry seasons, the first one “Verano” (June–September) much more pronounced than the second one “Veranillo” around December (Vuille et al., 2000).

As part of a reconnaissance in December 1999, a 16.5 m shallow ice core was drilled on Cumbre Ventimilla in order to investigate the suitability of the site to preserve (1) the climatic and environmental records, and (2) the seasonality of the signal. Since the shallow core revealed well-preserved signals, a deep drilling campaign was conducted one year later, in December 2000, and four ice cores were recovered. Three cores were drilled on Cumbre Ventimilla (54 m to bedrock, 40 m and 17 m), and one on the plateau located between both summits (Cumbre Ventimilla and Cumbre Whymper), which reached water saturated firn at 23 m depth. All cores were transported and preserved frozen until analyzes. In the same period, starting in October 1999 and continuing in 2000, the eruption of the adjacent volcano Tungurahua (5023 m, 1°47' S, 78°44' W) covered the Chimborazo glacier surface with a few mm thick ash layer. Whereas a smooth pure snow surface with only some hoarfrost structures was encountered in 1999 (Fig. 1a, with Tungurahua ash plume in the background), in 2000 the glacier was completely covered with meter high “ice penitents” enveloped with dark

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ash layers (Fig. 1b). Between July and December 1999, the volcanic emission of SO_2 increased to $10\,000\text{ t day}^{-1}$ and ash plumes reached $\sim 10\text{ km}$ altitude in 2000.

In order to study the influence of this volcanic eruption on the glaciochemical record, the 16.5 m core from 1999 (Core A) and the 17 m one from 2000 (Core B) were analyzed and compared. Core A and B were sub-sampled in 268 and 261 continuous samples, respectively, and analyzed for major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , F^- , and HCO_2^-), stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$), ECM (Core B only) using procedures described in Ginot et al. (2001) and Knüsel et al. (2002). H^+ was calculated from the ionic balance.

In this study, both ice core records were described and compared. Their comparison leads to the determination and discussion of each specific ion behavior under this volcanic perturbation, the control of the ionic budget conserved in the ice core column, and the definition of the adequate ionic ratio indicator related to the ice core evolution.

2 Ice cores records

2.1 Ice Core A – 1999

The general feature of the glaciochemical record is a strong seasonality of major ion concentrations and stable isotope ratios (Fig. 2). This is explained by the complex precipitation pattern on Chimborazo often resulting in a bimodal peak, similar to that observed in the previous study of stable isotope ratios in monthly composites of Ecuadorian precipitations (Garcia et al., 1998) and the Global Network for Isotopes in Precipitations (GNIP, IAEA, Vienna). A mean annual net-accumulation of 760 mm water equivalent (mm weq) was deduced, resulting in a time-span of the record of about 12 years (Ginot et al., 2002). The high concentrations of SO_4^{2-} , Cl^- , F^- , H^+ , Ca^{2+} and Mg^{2+} in the topmost 20 cm of the records (Fig. 2) are already due to input of volcanic material such as mineral acids (H_2SO_4 , HCl , HF) and fine volcanic ash (CaO , MgO), since the Tungurahua eruption started in October 1999. The seasonal variations reported from

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the stable isotopes allow the identification of the chemical species following the same seasonal pattern. Terrestrial salts coming with primary aerosols (Ca^{2+} , Mg^{2+} , SO_4^{2+} , CO_3^{2-}) are trapped in the snow by atmospheric scavenging or dry deposition (Delmas, 1992; Legrand and Mayewski, 1997) during wet and dry seasons respectively, and follow the hydrological bimodal cycles. Na^+ , Cl^- and K^+ , principal sea salt aerosol may show higher concentrations during the first rainy season (February–May) directly influenced by air masses originating in the Pacific. However, this relationship is not clearly marked in the record. NO_3^- , NH_4^+ and HCOO^- emitted from the biogenic activities and biomass burning reports high concentrations during both annual warm seasons according to the increase of local agriculture productivity and natural or human forest and field burning (“chaqueo”) (Legrand et al., 1992; Legrand and De Angelis, 1996).

2.2 Ice Core B – 2000

In order to compare the two ice core records, they had to be adjusted to account for the different sampling times. For this purpose the $\delta^{18}\text{O}$ records were used, assuming that they were least affected by surface melting and melt water percolation, resulting from lowering of the surface albedo due to the volcanic ash layer. This assumption is valid as long as the melt water percolates through the firn layers without refreezing until the impermeable firn-ice transition is reached. The $\delta^{18}\text{O}$ profile from Core A was used as reference and the Core B profile was stretched-shrunk in depth until best fit resulting in a 10% length reduction correction. The resulting records are shown in Fig. 2. The 150 mm weq shift of the Core B record surfaces reflects the net-accumulation between December 1999 and December 2000, which is significantly lower than mean annual net-accumulation of 760 mm weq. This deficit is explained by surface ablation/melting related to the volcanic event. Moreover, the upper part of the $\delta^{18}\text{O}$ record of Core B, between surface and 1 m weq depth, is drastically perturbed. This indicates that in addition to melting also partial refreezing of the melt water took place in this layer. Deeper, between 1 and 9 m weq, both records agree well. Thus, no significant melt water refreezing occurred in this section. The new depth scale for Core B was used for

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the comparison of both cores. The measured borehole temperature until 17 m depth ranged between -4.6 and -4.7°C .

All Core B chemical profiles are compared with those of Core A in Fig. 2. For NH_4^+ and NO_3^- both profiles A and B show the best agreement of all species. Apparent exceptions are the upper 1 m weq and the regions around 4.9 m weq depth (NH_4^+) and between 3–4.5 and 8.2–8.8 m weq depth (NO_3^-). In contrast to that, the Ca^{2+} , Mg^{2+} , SO_4^{2-} and F^- records in Core A and B show major differences. Between surface and 3.4 m weq depth, concentrations in Core B profiles are low, in the order of the background level from Core A, and the seasonal variation is no longer visible. At 3.3–4.4 m weq and 8.0–9.0 m weq depth, the highest concentration peaks appeared, also seen in H^+ . Between 4.4 and 8.0 m weq depth, the profile structures show some similarities, but with slightly higher concentrations in Core B. K^+ , Na^+ , Cl^- profiles from Core B are smoothed but conserved some similarities. The HCOO^- record B is disturbed down to 5 m weq depth, while it is well conserved in the deeper part.

3 Discussions

Volcanic emissions and deposition on the glacier surface started with the eruption of Tungurahua in July 1999 and peaked in September–October with ~ 9000 – $10\,000$ tons/day of SO_2 . The H_2SO_4 , HCl and HF depositions are well visible in the topmost 20 cm of Core A, which was recovered in December 1999. The main explosive phases of the volcano began in January 2000 with ash plumes rising to ~ 10 km altitude and tephra frequently blown to the West, the direction to Chimborazo glacier. This second phase decreased the surface snow albedo and followed by the dry season “verano” conditions were favorable to surface snow melting and sublimation. The 150 mm weq net-accumulation between December 1999 and 2000 compared with 760 mm weq mean annual net-accumulation suggests about 600 mm weq of ablation (melting and sublimation). Because of a relatively high firn temperature ($\sim -4.6^{\circ}\text{C}$),

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the melt water percolated through the entire firn layer without major refreezing, presumably down to the firn/ice transition at about 23 m depth (H. Bonnaveira, personal communication, 2001).

The eruption of volcano Tungurahua had multiple effects on the Chimborazo glacier. The first effect, visible on the surface, was the deposition of dark volcanic ash between October 1999 and December 2000 that lowered surface snow albedo. The lower albedo induced surface snow melting and sublimation, resulting in the formation of “ice penitents” visible in Fig. 1. The second effect was the input of the acids H_2SO_4 , HCl and HF as well as volcanic ash containing CaO and MgO . The third effect was the percolation of melt water, containing high concentrations of soluble ions of volcanic origin, through the entire firn layer. The melt water pulse caused an input of certain ions into the firn layer, but was also responsible for preferential elution and relocation of ions originally present in the firn.

3.1 Preferential elution of ions

As demonstrated by previous studies (Davies et al., 1982; Hou and Qin, 2002; Pohjola et al., 2002; Grumet et al., 1998; Brimblecombe et al., 1985; Tsiouris et al., 1985; Eichler et al., 2001), strong acids, and H_2SO_4 in particular, are preferentially eluted by melt water because the corresponding ions are expected to be enriched at firn grain boundaries. In our case, the highest SO_4^{2-} concentration peak observed in Core A between surface and 1 m weq depth related to volcanic deposits, and the usual seasonal concentration variability down to 3.3 m weq depth, were completely removed in Core B; the mean concentration decreased from 3.88 to 1.88 $\mu\text{Eq L}^{-1}$ for this section (Table 1). This section of the snowpack is followed by a segment where SO_4^{2-} appeared in two peaks between 3.3 and 4.4 m weq depth, showing the highest concentrations in entire Core B with a mean of 22.34 $\mu\text{Eq L}^{-1}$. It is not clear which process dominated this relocation in an area with originally low concentrations in Core A. Hou and Qin (2002) suggested that percolating highly concentrated melt water refroze on top of impermeable ice layers formed in the previous summer, which act as physical obstacle against

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melt water percolation. However, such ice layers were not present in Core A and, in addition, there is no indication of a major refreezing in the $\delta^{18}\text{O}$ record. In the considered section, density increases from 0.44 to 0.55 g cm^{-3} and reaches a major stratigraphic change with the end of the first stage of densification (Herron and Langway, 1980), where the dominant mechanism is considered to be grain settling and packing. Probably the re-deposition of SO_4^{2-} in this region is related to the stratigraphic transition. Between 4.4 and 8.1 m weq depth, some structures from Core A are conserved in Core B, but with additional peaks and a higher background (Table 1). In the deepest part of the record between 8.1 and 9 m weq a second relocation zone was observed, where Core B mean SO_4^{2-} reached 24.51 $\mu\text{Eq L}^{-1}$ in comparison with the 3.33 $\mu\text{Eq L}^{-1}$ in Core A.

H^+ , F^- , Ca^{2+} , and Mg^{2+} show similar behavior than SO_4^{2-} . The tendency of Ca^{2+} and Mg^{2+} to be eluted and relocated easily was already observed in previous studies (Davies et al., 1982; Tsiouris et al., 1985; Eichler et al., 2001). This observation was explained by exclusion of these ions from the ice lattice into boundary regions during grain growth, which makes them accessible for percolating melt water (Eichler et al., 2001). This exclusion process might even be more effective on Chimborazo, since Ca^{2+} and Mg^{2+} originating from local terrestrial salts, are preferentially incorporated in the snow pack during the dry seasons by dry deposition. Leaching of Ca^{2+} and Mg^{2+} in the volcanic ash layer is facilitated by the acidic conditions, resulting in a similar elution and relocation behavior than observed for SO_4^{2-} (see Table 1). F^- seems to be less affected by relocation; at least in the upper part of Core B (1–3 m weq depth) the original structure is preserved. This is consistent with previous studies, suggesting high solubility of F^- in ice and accordingly a low susceptibility against elution (Eichler et al., 2001). However the overwhelming effect in the Chimborazo record is the volcanic F^- input with the melt water pulse, most probably in form of HF. Interestingly, this additional F^- is redeposited in the same core regions as SO_4^{2-} , Ca^{2+} , and Mg^{2+} (Table 1).

NH_4^+ is the best preserved ion as indicated by the good correspondence between Core A and B, in agreement with previous studies (Eichler et al., 2001; Pohjola et al.,

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Core A and B are 3.21 and 9.17 mg cm^{-2} , respectively. This difference is attributed to the additional input due to the volcanic activity. Between December 1999 and 2000, the eruption of Tungurahua continued to deposit these species on the glacier surface and the volcanic activity was particularly high in the year 2000. Since melt water drainage occurred (see below), the total volcanic input cannot be determined. In the flux curves in Fig. 2b, the initial surface input is characterized by the rounded start of the Core A curve, and the redeposition layers in Core B, by the inflection of the curves at 3.3 and 8.1 m weq depth.

The second group of species, Na^+ , K^+ and HCOO^- , showed higher total fluxes in Core A, e.g. the Na^+ flux decreased from 1.79 mg cm^{-2} in 1999 to 0.92 mg cm^{-2} in 2000. This can only be explained by the fact that melt water percolation was not stopped at the deepest part of Core B, but instead melt water drainage occurred. As we know from the drilling performed on the pass between the two Chimborazo summits, a huge quantity of liquid water was stored above the firn/ice transition at about 23 m depth. It seems that the surface melt water on Chimborazo Cumbre Ventimilla, where Cores A and B were recovered, percolated through the entire firn layer until reaching the ice interface, and drained down to the lower pass. This drainage must have affected ions of group one as well, but there it was overcompensated by the volcanic input.

The last group of species consists of NH_4^+ and NO_3^- . As discussed above, these species are less affected by elution and redeposition processes and accordingly the total accumulated deposition flux curves from Core A and B agree reasonably well.

3.3 Ionic ratios

The examination of ionic ratios between species exhibiting different behaviors allows a better characterization of these elution and migration processes. The $\text{SO}_4^{2-}/\text{NH}_4^+$ ratio (Fig. 3) compares two ions with opposite position in the elution sequence. The ratio is quite constant with a mean of about 0.40 under 1 m weq depth but with higher values in the first meter under surface. This indicates well the sulfate excess stored in

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the upper meter corresponding to the recent volcanic input. For Core B, the sulfate excess is shifted under 3 m weq depth into several layers, the much concentrated located between 3.3 and 4.4 m weq depth. The $\text{SO}_4^{2-}/\text{NH}_4^+$ ratio can therefore be used as marker for sulfate excess. A previous study from Iizuka et al. (2002) presents the ratio of $\text{Mg}^{2+}/\text{Na}^+$ as indicator of seasonal melting in an ice core from Svalbard. This method was applied for Chimborazo record and illustrated in Fig. 3. The results are different and rather help to define the core sections where Mg^{2+} (or Ca^{2+}) re-depositions take place with ratios of ~ 2 . Ca^{2+} and Mg^{2+} react together under the elution process and their ratio confirms this identical position in the elution sequence. Both $\text{Mg}^{2+}/\text{Ca}^{2+}$ profiles did not report marked changes all over the cores confirming their identical behavior in normal, elution or re-deposition phases. The slight lower ratio between Core B and A informs that the Ca^{2+} elution factor is a little bit higher than Mg^{2+} . The last discussed ratio is Cl^-/Na^+ . If Na^+ and Cl^- are incorporated together in the snow flakes as condensation nuclei aerosol originating only from sea salt, their ratio is close to 1.16 (dashed line in Fig. 3) (Keene et al., 1986). However, the mean ratio observed in Core A between 1 and 9 m weq depth is 0.91 indicating an additional but constant Na^+ input, when the high ratio close to the surface is related to the Cl^- excess coming from the volcanic HCl deposition. In Core B, the Cl^-/Na^+ ratio reports high fluctuation between 1 and 12 indicating that the Cl^- volcanic excess was eluted and diffused all over the core without preferential layers like for other strong acids.

4 Conclusions

In 1999 and 2000, two shallow ice cores were recovered on the same place from the summit of Chimborazo. In the same period, the eruption of the proximate Tungurahua volcano reaches the height of its power and covers the neighborhood and the Chimborazo glacier with ash and acid deposits. The comparison of both ice cores allows to follow the impact of these perturbations on the ice core chemistry and to investigate the processes of isotopic and ionic elution and re-localization involved. Only the

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upper meter from the record shows some changes in the stable isotopes records indicating that water melted from the surface refreeze and is stored in that upper section. Below, until 9 m weq depth, melt water only percolates through firn layers, without re-freezing. Some ions exhibits strong elution and re-localization like others seems to be less mobile under the effect of surface water percolation, leading to elution sequence: $\text{SO}_4^{2-} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{F}^- > \text{Na}^+ = \text{K}^+ > \text{Cl}^- > \text{NO}_3^- > \text{HCOO}^- = \text{NH}_4^+$. The comparison between both cores reveals also the major volcanic eruption input of Ca^{2+} , Mg^{2+} , F^- , Cl^- , and SO_4^{2-} , first deposited on the glacier surface snow in 1999 and eluted and re-deposited deeper in 2000. Species integrated in the snowpack by exceptional event like volcanic eruption or stocked on the surface snow flakes by atmospheric scavenging are preferentially flushed out and re-deposited in deeper preferential layers. Nevertheless, for Na^+ , K^+ and HCOO^- , the comparison shows that one fraction of these species is lost with the loaded percolating water or re-deposited deeper. The complete analyzes of the other 54 m parallel ice core also recovered in 2000 and reaching bedrock should bring complementary information.

Concerning the potential of Chimborazo ice cores to reconstruct past environmental and climatic conditions, it depends to the frequencies of such volcanic perturbation. As we know, Tungurahua is one of Ecuador's most active volcanoes. Prior to a long-term eruption beginning in 1995 that caused the temporary evacuation of the city of Baños at the foot of the volcano, the last major eruption had occurred from 1916 to 1918, although minor activity continued until 1925. The time span covered by the 54 m long ice core should cover the 20th century, so that some portions of the record may conserve their original composition. Otherwise, the available unperturbed proxies are reduced to stable isotopes and some ionic species (NH_4^+ , NO_3^- , HCOO^- ?). On the other hand, the stratigraphical examination of the 54 m core reveals a large number of ash layers mostly observed in the deepest 20 m (~70 layers, H. Bonnaveira, personal communication, 2001) that could indicate that the time range covered by this core may be longer.

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Table 1. Mean concentrations ($\mu\text{Eq L}^{-1}$) for core A and B sections (depth in m weq). Bold values indicate major redeposition sections.

	0–3.3		3.3–4.4		4.4–8.1		8.1–9.1	
	Core A	Core B	Core A	Core B	Core A	Core B	Core A	Core B
NH_4^+	6.17	5.07	6.82	5.44	8.96	5.45	10.66	7.43
Ca^{2+}	3.53	1.75	3.19	12.00	5.22	5.72	5.48	15.08
Mg^{2+}	0.74	0.42	0.60	4.10	0.87	1.93	1.29	6.34
K^+	0.96	0.34	0.93	0.70	0.72	0.36	1.14	0.88
Na^+	2.28	0.92	1.84	1.24	1.82	0.56	1.61	2.16
F^-	0.38	0.42	0.56	2.32	0.40	0.63	0.39	2.35
Cl^-	2.56	3.91	1.14	3.95	1.21	2.01	1.65	8.35
NO_3^-	2.17	1.60	1.78	3.39	2.28	2.40	2.23	4.31
SO_4^{2-}	3.88	1.73	2.04	22.99	3.09	8.18	3.33	25.12
HCOO^-	2.57	1.75	6.64	2.52	4.84	3.01	3.57	2.24

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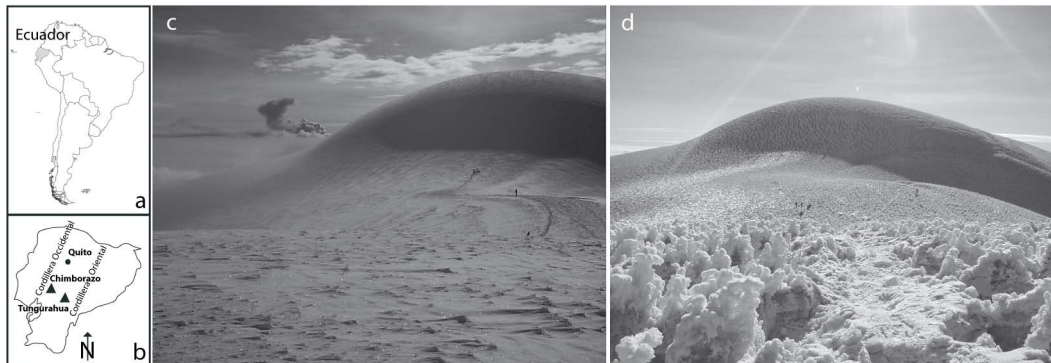


Fig. 1. Map of South America **(a)** and Ecuador **(b)**, showing the location of Chimborazo and Tungurahua summits. Views of Chimborazo Cumbre Whymper (6268 m) and middle plateau from Cumbre Ventimilla (6230 m) in 1999 **(c)** and 2000 **(d)**. A smooth snow surface was encountered in December 1999, whereas the Tungurahua eruption (ash plume visible in the background) transformed the glacier surface, which was completely covered with ash, penitents and hoarfrost in December 2000.

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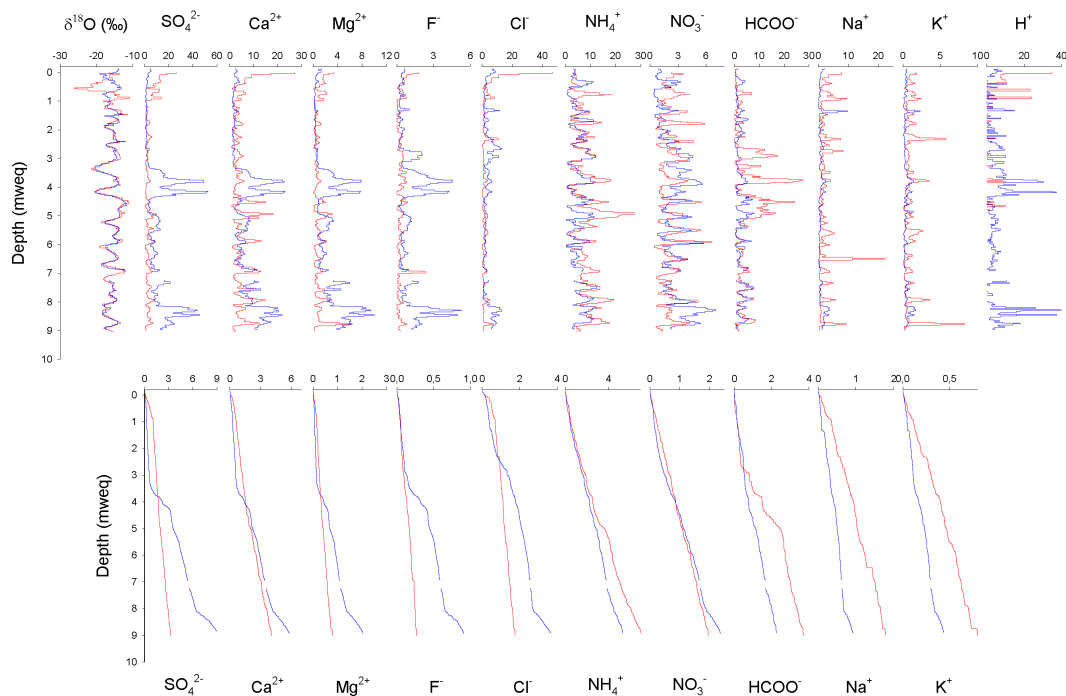


Fig. 2. (a) Comparison of $\delta^{18}\text{O}$ and major ion concentration profiles recorded in core A (1999, red line) and B (2000, blue line). Ion concentrations are in $\mu\text{Eq L}^{-1}$. (b) Accumulated deposition fluxes of the different ions (in mg cm^{-2}).

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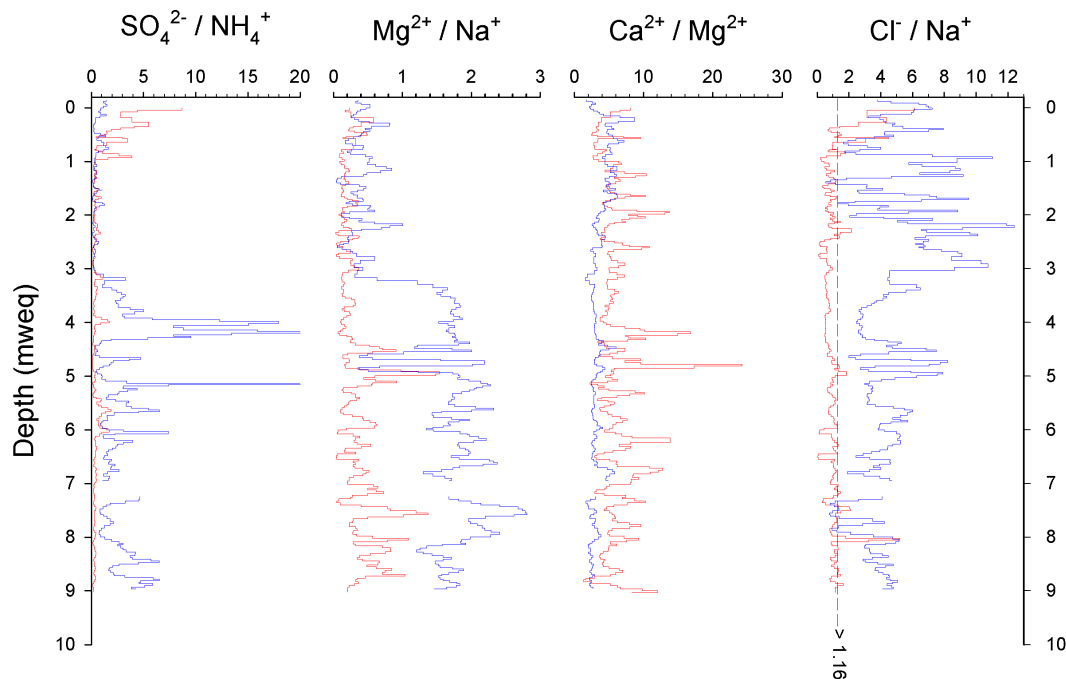


Fig. 3. The selected ionic ratios profiles for both Chimborazo ice cores (red line for Core A, blue line for Core B) illustrate the preferential elution and re-localization of some ionic species. For $\text{Cl}^- / \text{Na}^+$, the dashed line at 1.16 represent the sea salt ratio from Keene et al. (1986).

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